Potential for visualising ultrafast structural changes in solution

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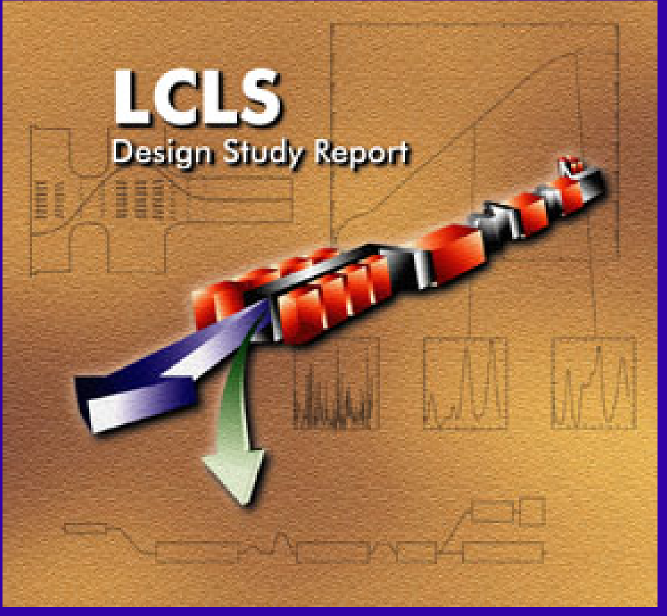
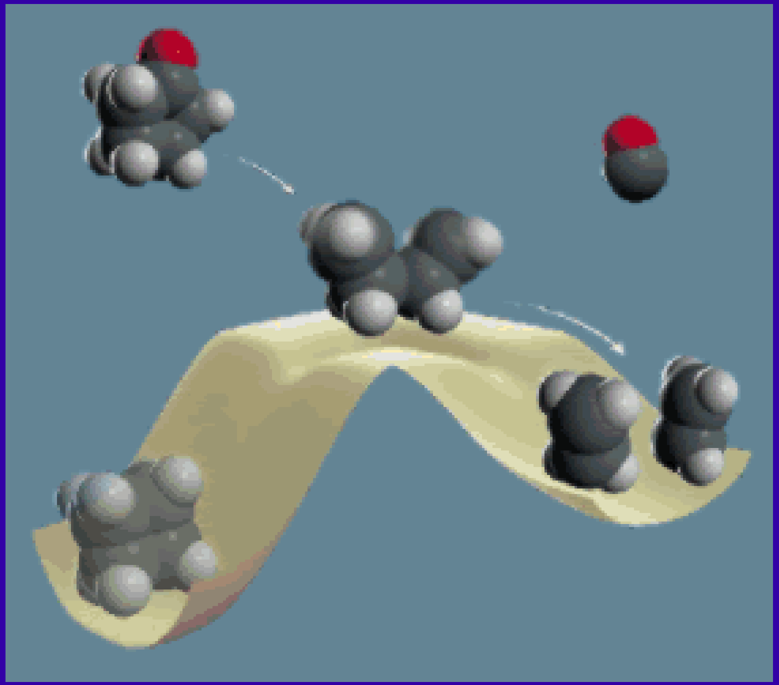


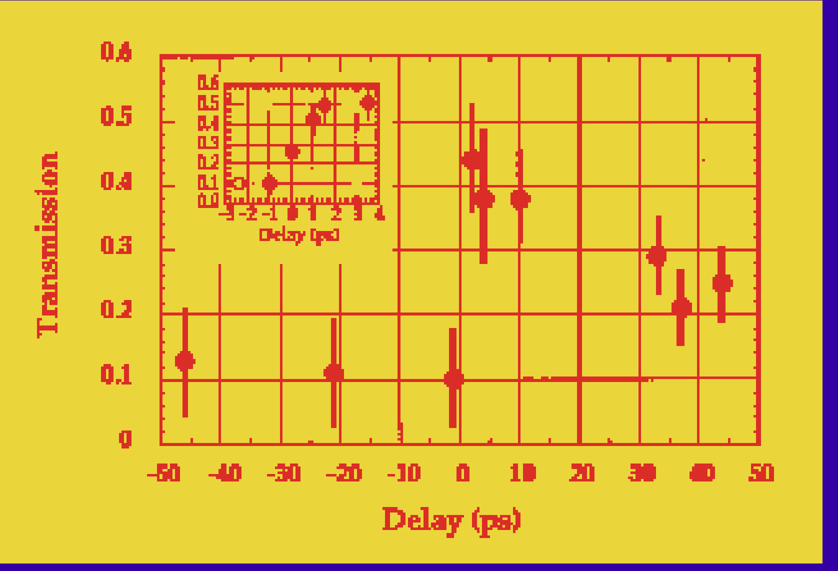
Scientific Motivation



- Spectroscopy probes transitions between energy surfaces.
  - Must chart all accessible surfaces.
  - Unique interpretation problematic as complexity increases.
  - Thermal artifacts.
- Structure based pump-probe methods complementing fs spectroscopy potentially powerful.

Picosecond XAS

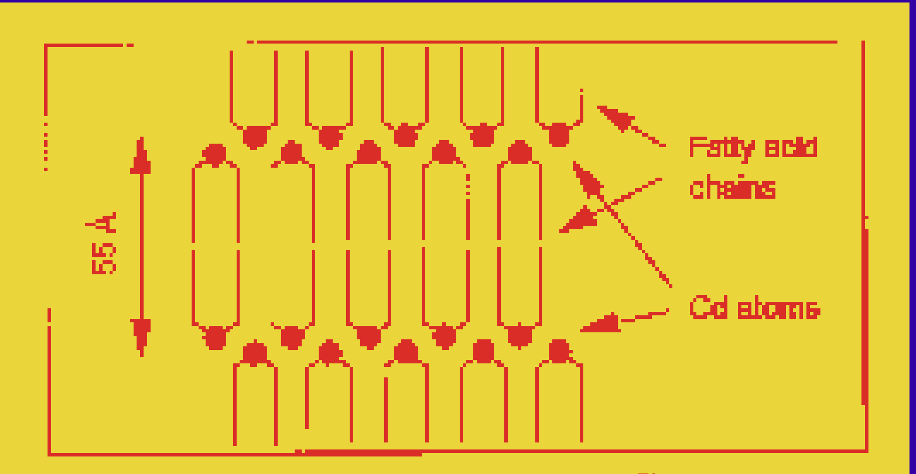
- Laser produced X-ray plasma source.
- Near edge absorption of SF_6 gas.
  - High-symmetry enhances K-edge ionisation cross-section.
  - Resonance disappears as SF_6 dissociates.



- $\sim$ 1 ps temporal resolution.
  - Ráksi *et al.*, J. Chem. Phys. (1996).

Sub-picosecond Multi-layer Diffraction

- Laser plasma X-ray probe.
- Langmuir-Blodget film.
  - Highly ordered & enables multilayer diffraction.
  - Rapidly disorders upon heating.



Structure of Langmuir-Blodgett film

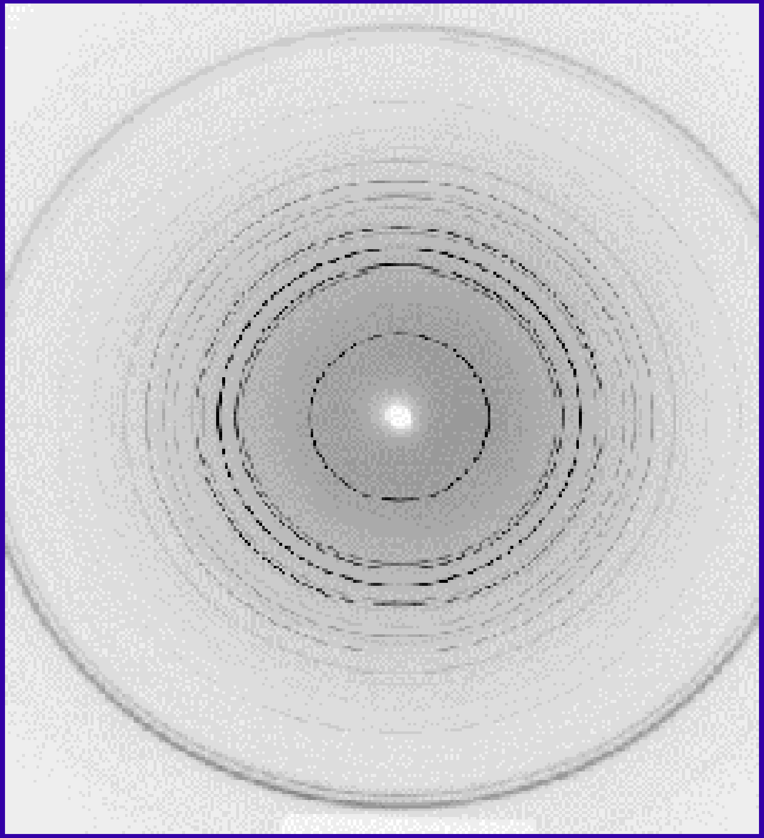
- $\sim$ 1 ps temporal resolution.
  - Rischel *et al.*, Nature (1997).

Picosecond Powder Diffraction

- Monochromatic synchrotron radiation.

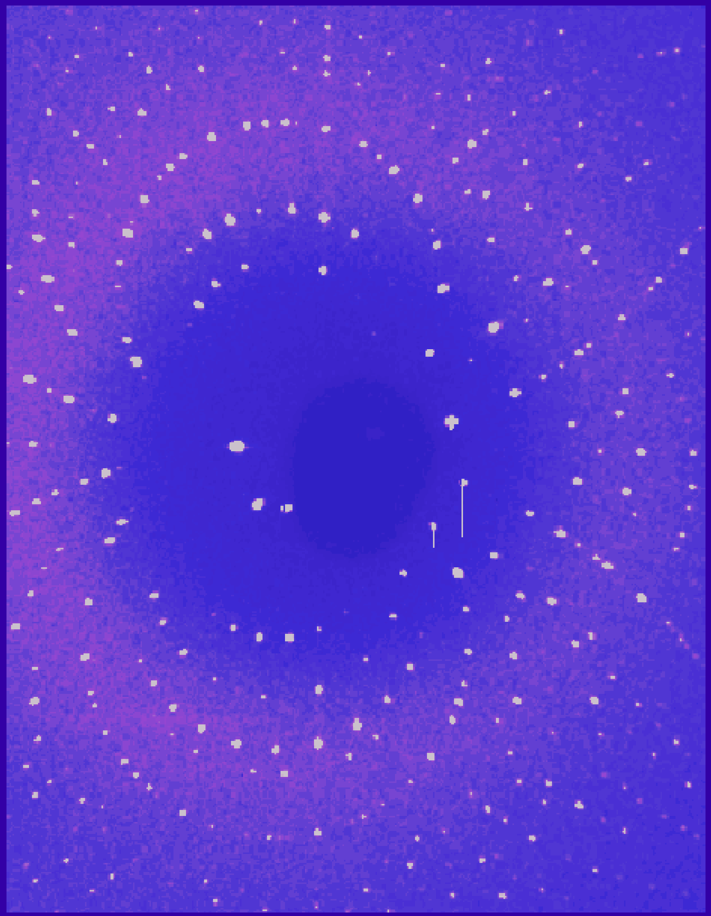
- N,N-dimethylaminobenzonitrile.
  - Diffraction quality powders.
  - Numerous diffraction peaks sampled simultaneously.
  - Detailed structural information.

- $\sim$ 80 ps temporal-resolution.
  - Techert *et al.*, Phys. Rev. Lett. (2000).



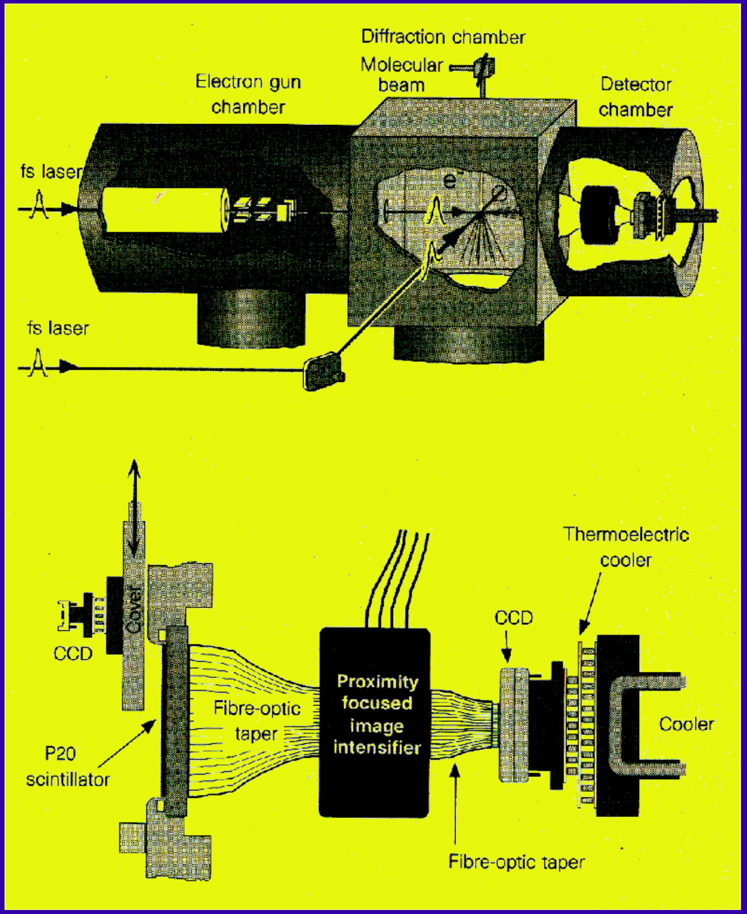
Nanosecond Laue Diffraction

- White synchrotron beam.
- Photolysis of MbCO.
  - Small ligand photo-dissociation & recombination reaction.
  - Sensitive to disordering.
- $\sim$ 7 ns temporal resolution.
  - Srajer *et al.*, Science (1996).



Picosecond Electron Scattering

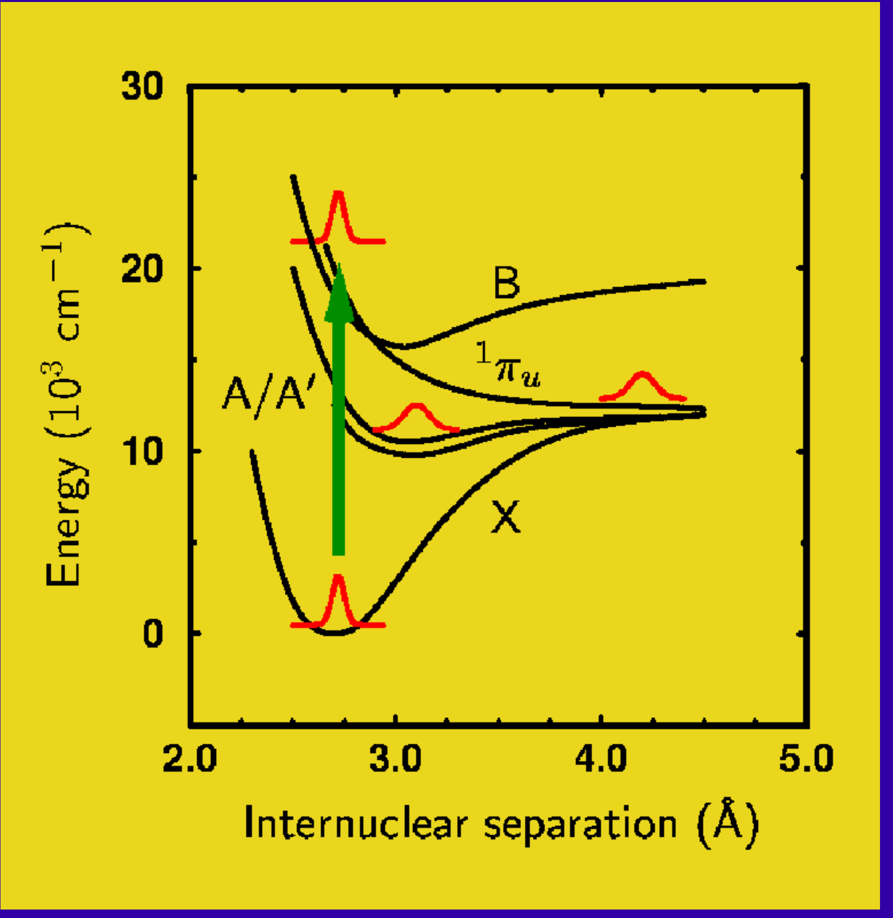
- Pulsed electron beam.
- CH_2I_2 as prototype system.
  - Vacuum phase dissociation reaction.
  - Signal-to-noise challenging.
- $\sim$ 10 ps temporal-resolution.
  - Williamson *et al.*, Nature (1997).



Iodine's Photochemistry in Solution

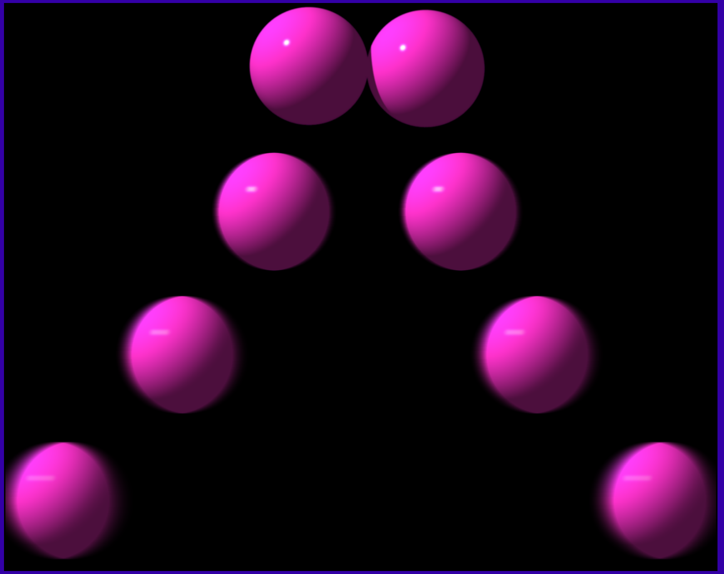
$$I_2 + h\nu \rightarrow I + I \rightarrow I_2^* \rightarrow I_2$$

- Photo-dissociation.
- Solvent caging (< 2 ps).
- Geminate recombination & vibrational relaxation.
- Excited state lifetime ≈ 500 ps in CH_2Cl_2.



Historical Milestones

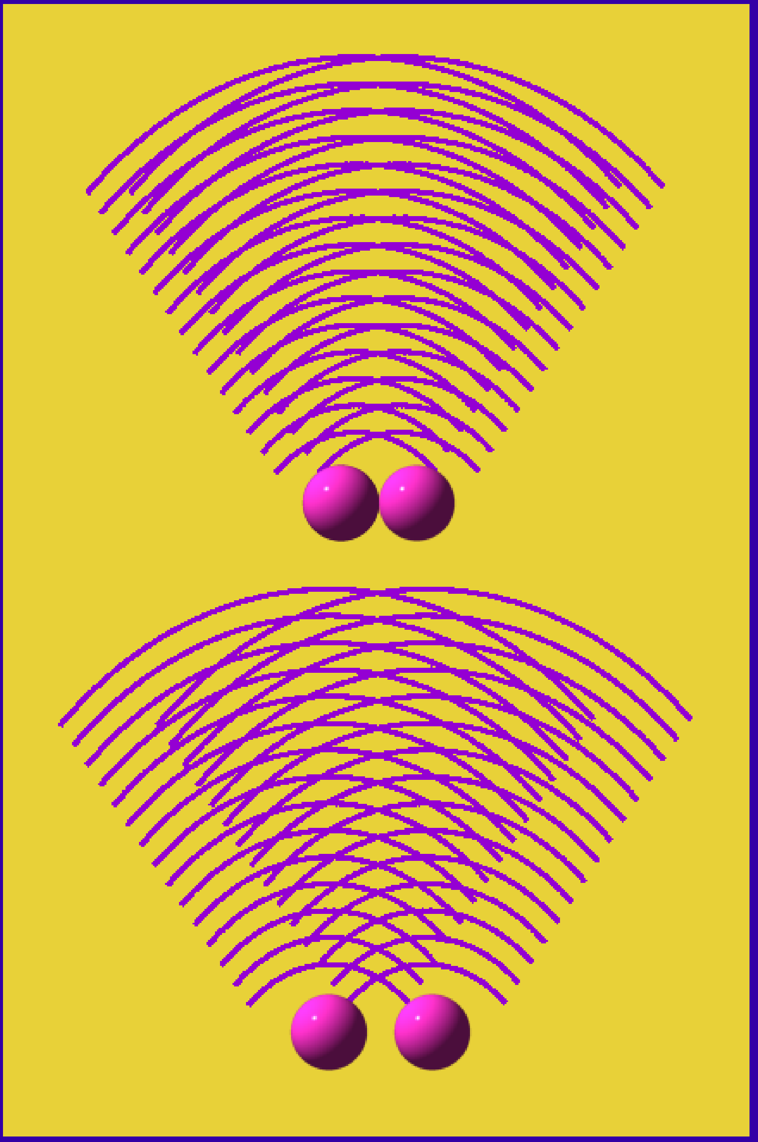
- Rabinovitch & Wood (1936):
  Proposed solvent enhanced geminate recombination.



- Chuang, Hoffman & Eisenthal (1974):
  Picosecond pump-probe experiment.
- Smith & Harris (1987):
  Consensus picture.
- Bergsma *et al.* (1986):
  Simulated a time-resolved diffuse X-ray scattering experiment.

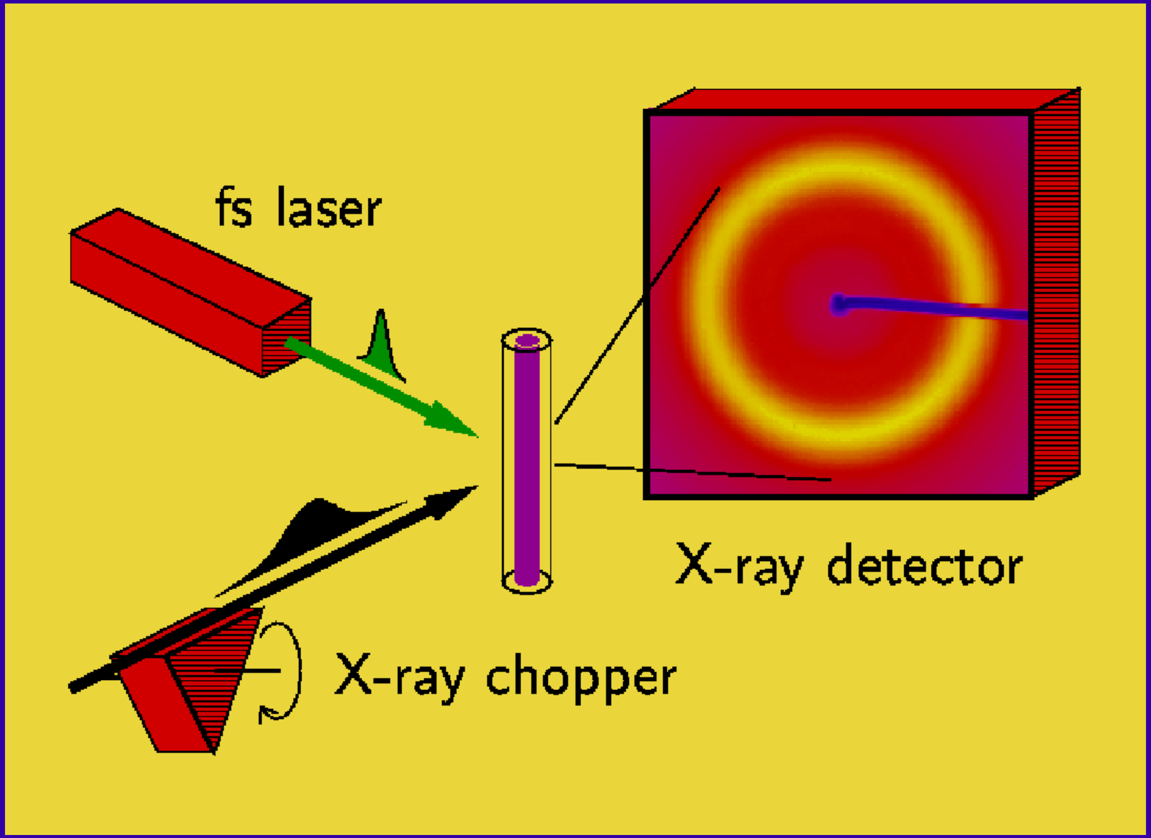
Diffuse X-ray Scattering

- X-ray scattering dependent upon atomic spacing.
  - Perturb bond-lengths & perturb scattering.
- In solution average over all orientations.

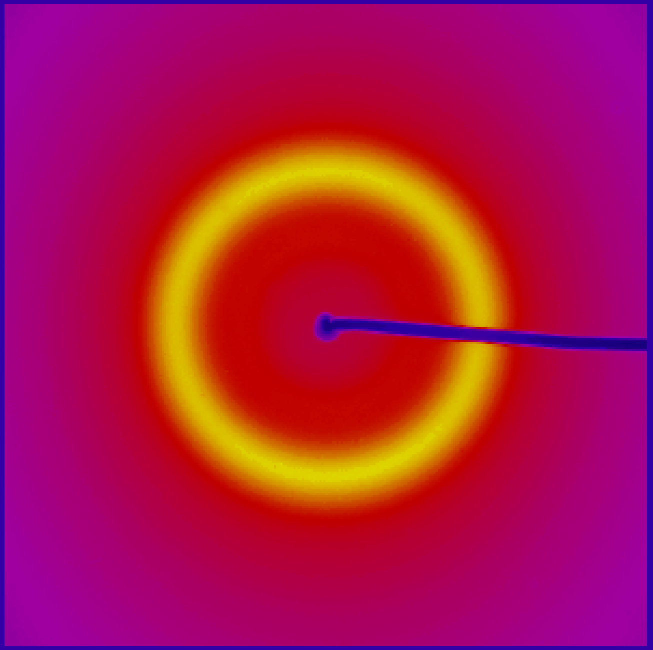


Pump-probe X-ray Experiment

- 40 mMol I_2 in CH_2Cl_2.
- 25 μJ per 100 fs pulse.
- Monochromatic 80 ps X-ray pulses @ ESRF.
- CCD camera.
  - 15 minutes/exposure.



Analysis

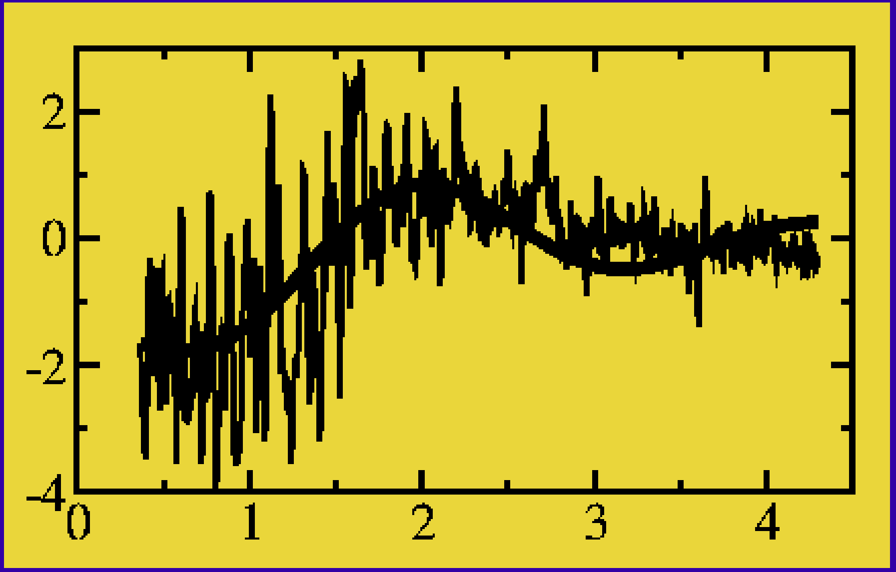


→ Integrate in Rings

↓

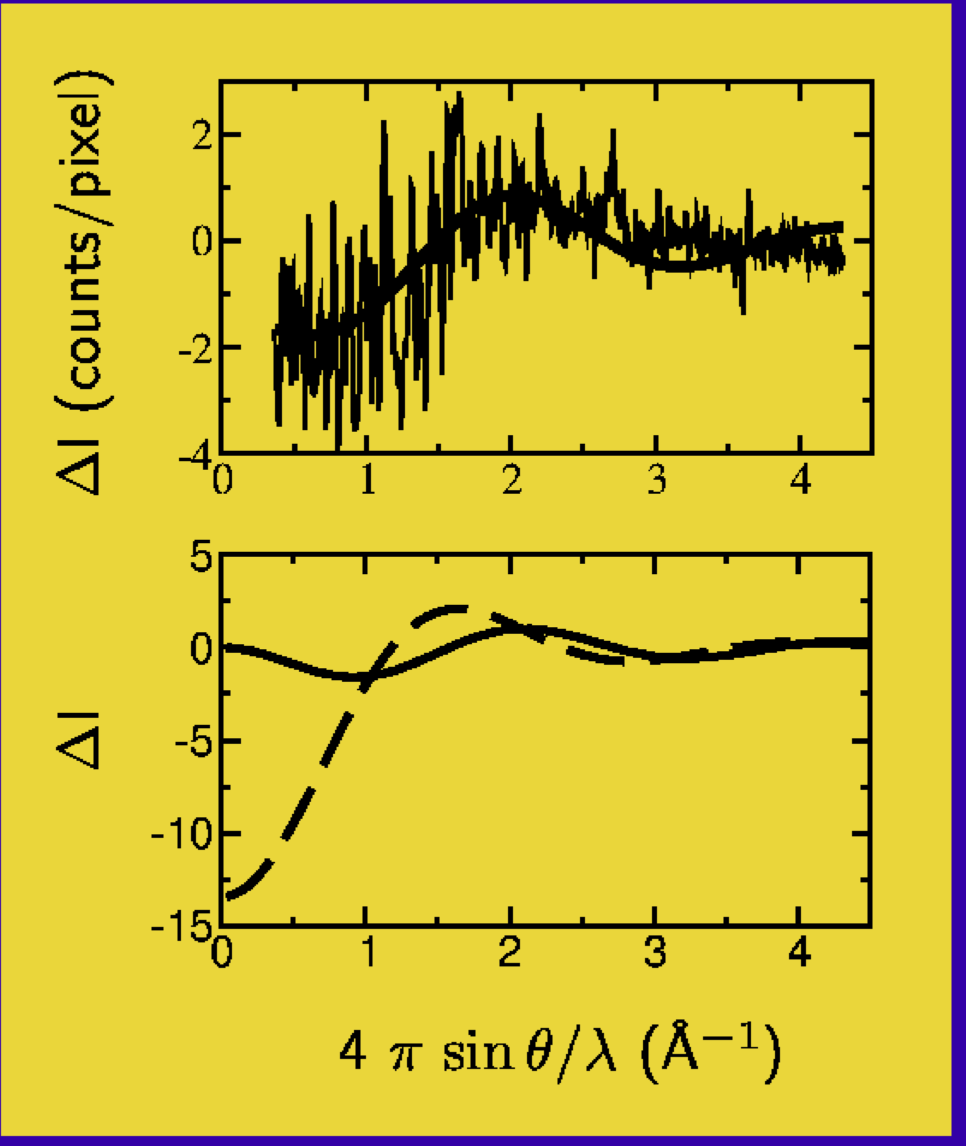
Subtract “laser off” from “laser on”

↓



Experimental Result

- Laser on vrs. Laser off.
  - Change in diffuse X-ray scattering observed.
  - $\sim$ 30 % yield.
  - $\sim$ 15 % of product escaped the cage.



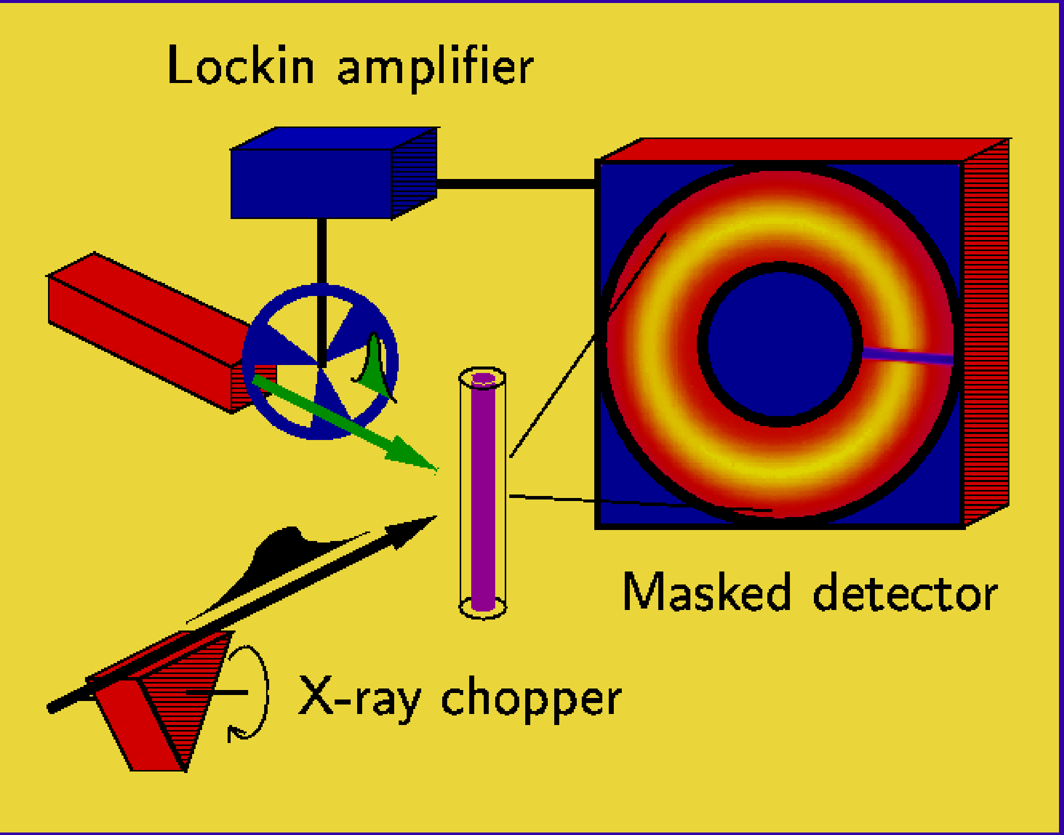
Summary

- $\Delta I/I \approx 2 \times 10^{-3}$.
  - Near the CCD camera's limits.
  - High Q information missing.

- Geminate yield: 25 %.
  Non-geminate yield: 5 %.
- Change in Atomic spacing 0.4 Å± 0.2 Å.
- Proof of principle but not a time-resolved experiment.

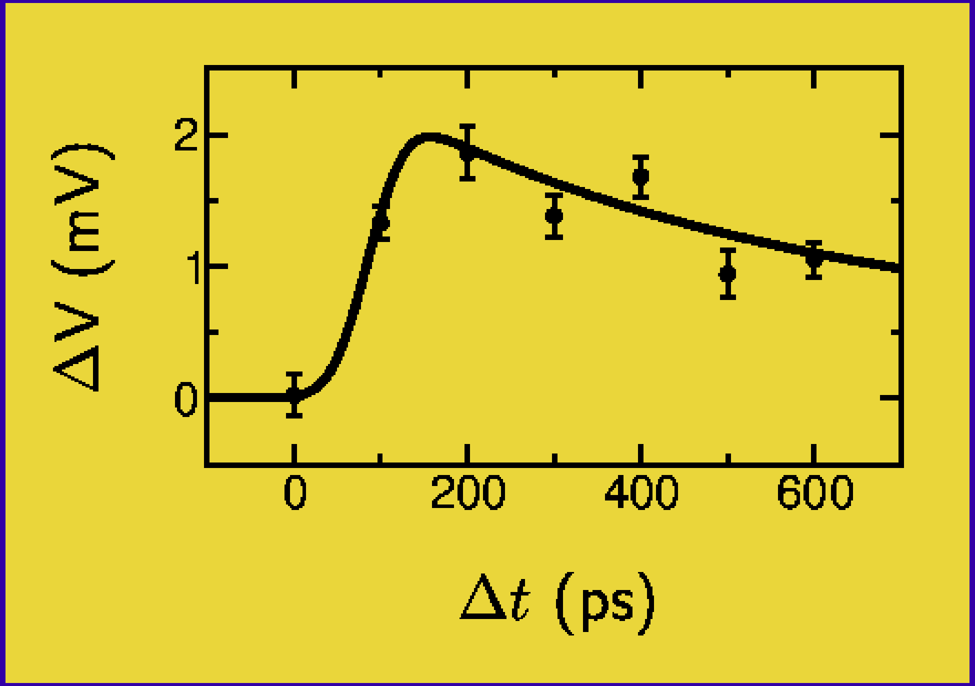
Lock-in Detection Experiment

- 40 mMol I_2 in CH_2Cl_2.
- 20 μJ per 100 fs pulse.
- Monochromatic 80 ps X-ray pulses @ ESRF.
- Gas filled detector & apply lock-in technique.



Experimental Result

- Laser on vrs. Laser off.
  - Change in diffuse X-ray scattering observed.
  - $\sim$ 500 ps time constant.



Summary

- Time-resolved signal recoverable.
- Limited by X-ray flux.
  - Use 1 % bandwidth X-ray optics.
- Laser & X-ray overlap critical.
  - Higher laser flux.

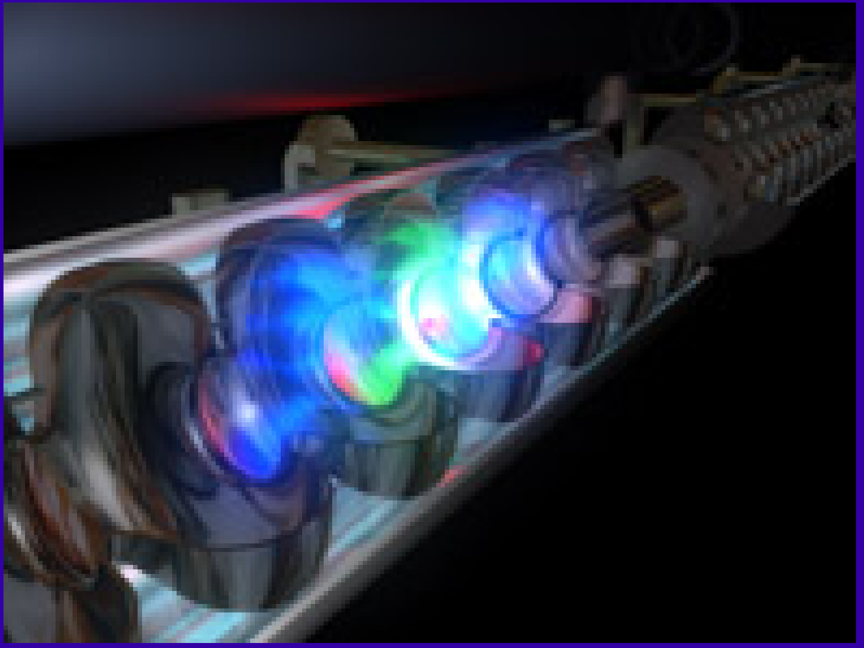
- One-dimensional experiment.
  - Multi-ring detector & simultaneously follow dynamics & diffuse scattering profile.

4th Generation X-ray Sources

- 100 fs X-ray pulses.
  - Domain of ultrafast photochemistry.
- $\sim 10^{12}$ photons/pulse within ~ 1 % bandwidth.
  - Eight orders of magnitude improvement on this experiment.
  - Improve signal to noise.
  - Reduce integration times.
  - More complex systems.

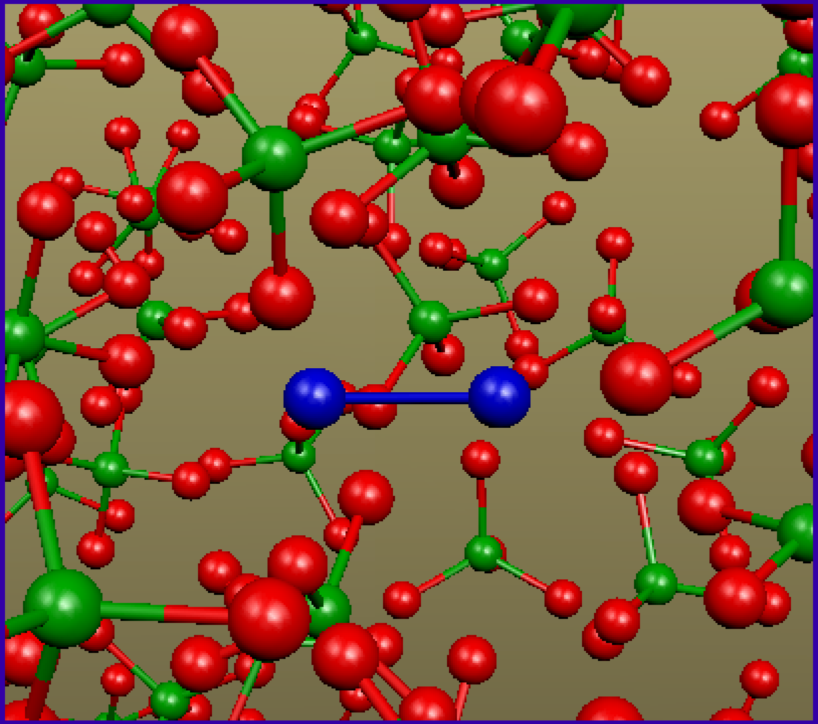
Technical Experimental Targets

- Pulse length $\leq$ 100 fs.
  - Synchronization?
  - Time arrival & read detector every pulse?
- 10^{12} photon/pulse @ 100 Hz.
  - Resolve $\Delta I/I \leq 10^{-4}$.
  - Detector stability?
  - An enclosed flow cell/detector.
- Beam stability.
  - Seeding?
  - Spectrally resolve every pulse?



Proof of Principle Experiment

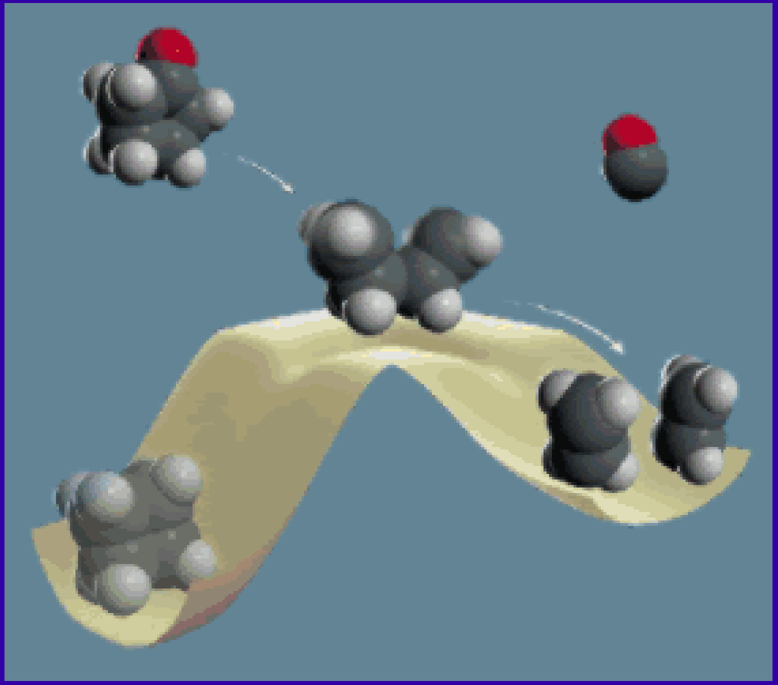
- I_2 in ethelyene glycole.
  - Absorption max $\approx$ 400 nm.
  - Solvent caging $\approx$ 600 fs.
  - Vibrational relaxation $\approx$ 20 ps.



- Scientific interest:
  - Clock solvent cage formation.
  - Follow cage-breakout.
  - Coherent reaction dynamics in solution (oscillation period $\approx$ 300 fs).

More Complex Structural Dynamics

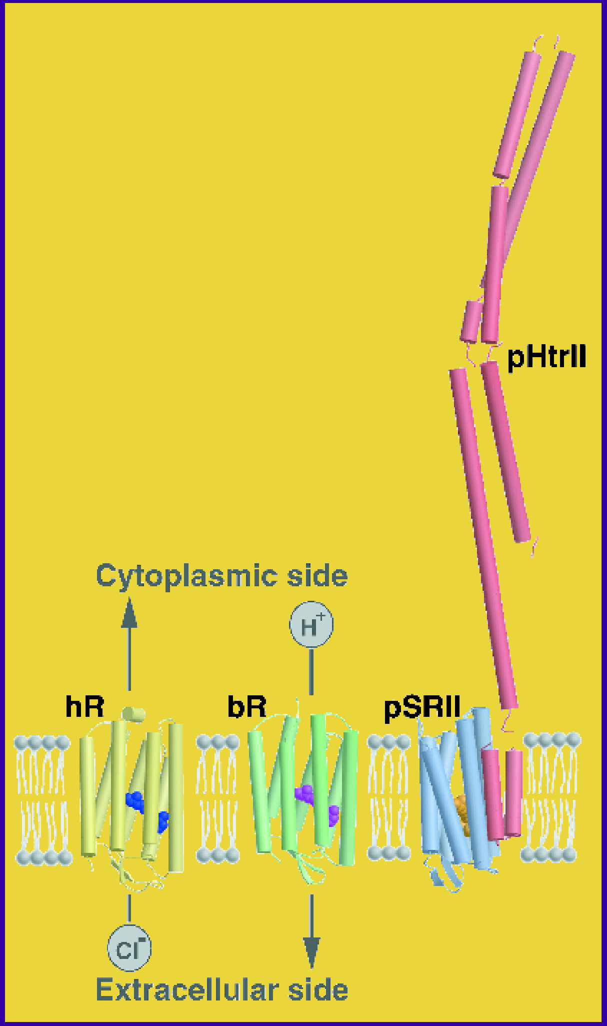
- A kaliediscope of photoactive small-molecules.
  - Unambiguous structural signal.
  - Complement fs spectroscopy.



- Scientific interest:
  - Distinguish reaction pathways.
  - Branching ratios.
  - Influence of solvent.

Membrane Proteins

- Semi-ordered X-ray scattering.
  - Stacked bilayers.
- Halorhodopsin.
  - Visualise chloride pumping.
- Bacterial Reaction Centres.
  - Coherent low frequency motions observed.
  - Coupled to electron transport?
  - Structurally characterise these motions.



Conclusions

- State of the Art.
  - Transient structural changes in solution observable with $\sim$ 100 ps resolution.
- Impact of an X-ray FEL.
  - Dramatically improve temporal resolution & signal-to-noise.
  - Detector & sample stability crucial.
  - Potential for exciting science.

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